



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 544 340 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:

02.10.1996 Bulletin 1996/40

(51) Int Cl.⁶: **C08F 210/02, C08F 4/655**

(21) Application number: **92202085.4**

(22) Date of filing: **08.07.1992**

(54) Process for the preparation of elastomeric copolymers of ethylene

Verfahren zur Herstellung von Elastomer-Ethylencopolymeren

Procédé de préparation de copolymères élastomères d'éthylène

(84) Designated Contracting States:

AT BE CH DE DK ES FR GB GR IT LI LU MC NL
PT SE

(30) Priority: **25.11.1991 IT MI913140**

(43) Date of publication of application:
02.06.1993 Bulletin 1993/22

(73) Proprietor: **ENICHEM ELASTOMERI S.r.l.**
I-20121 Milan (IT)

(72) Inventors:

• **Tanaglia, Tiziano**
I-40139 Bologna (IT)

• **Foschi, Sergio**
I-44100 Ferrara (IT)

(74) Representative: **Fusina, Gerolamo et al**
Ing. Barzanò & Zanardo Milano S.p.A,
Via Borgonuovo, 10
20121 Milano (IT)

(56) References cited:
EP-A- 0 243 327 **EP-A- 0 281 524**
EP-A- 0 522 650

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Description

The present invention relates to a process for the preparation of elastomeric copolymers of ethylene.

More specifically, the present invention relates to a process for the preparation of elastomeric copolymers of ethylene, wherein the ethylene is copolymerized with an α -olefin, and possibly with a diene, in the presence of a Ziegler-Natta catalyst including a solid component of catalyst based on titanium and aluminium, supported on magnesium chloride.

It is well-known in the art that for an ethylene/ α -olefin copolymer to be considered as being elastomeric, the distribution of comonomers along the chain must be alternated as much as possible, to prevent the formation of long ethylenic sequences, which would cause an increase in the crystallinity and consequently a decrease in the elastic properties.

Moreover, to lower the degree of crystallinity, the polymeric material must have a narrow distribution of composition, to avoid the presence of fractions having a high content of ethylene.

It is also known that ethylene can be polymerized with α -olefins using a low pressure procedure on Ziegler-Natta catalysts. These catalysts are generally composed of a compound of transition elements belonging to groups IVb, Vb or VIb of the periodic Table, mixed with an organometallic compound, or hydride, of the elements from groups I to III of the Periodic Table.

Solid components of Ziegler-Natta catalyst are known in the art, containing a transition metal (generally titanium), a bivalent metal (generally magnesium), a halogen (generally chlorine) and possibly also an electron donor. These solid components, combined with an organometallic compound of aluminium, form highly active catalysts in procedures for the (co)polymerization of ethylene carried out at low temperature and pressure.

U.S. Patent 3.642.746, for example, describes a solid component of catalyst obtained by the contact of a compound of a transition metal with a halide of a bivalent metal treated with an electron donor. According to U.S. Patent 4.421.674, a solid component of catalyst is obtained by the contact of a compound of a transition metal with the product of a spray-dried solution of magnesium chloride in ethanol. According to U.K. Patent 1.401.708, a solid component of catalyst is obtained by the interaction of a magnesium halide, a non-halogenated compound of a transition metal and an aluminium halide. U.S. Patents 3.901.863 and 4.292.200 describe solid components of catalyst obtained by putting a non-halogenated magnesium compound in contact with a non-halogenated compound of a transition metal and an aluminium halide.

U.S. Patent 4.843.049 describes a solid component of catalyst which contains titanium, magnesium, aluminium, chlorine and alkoxy groups, obtained by spray-drying an ethanol solution of magnesium chloride to obtain an active support, which is interacted in sequence with a titanium tetra-alkoxide and an alkyl aluminium chloride.

It has now been found, in accordance with the present invention, that it is possible to obtain, with high yields, elastomeric copolymers of ethylene with α -olefins, and possibly with a diene as termonomer, having a low crystallinity even with a high content of ethylene, by means of a copolymerization process using a Ziegler-Natta catalyst with a similar composition to that described in U.S. Patent 4.843.049, prepared according to a special procedure, as described hereafter.

The present invention consequently relates to a process for the preparation of elastomeric copolymers of ethylene, wherein ethylene is copolymerised with an α -olefin, and possibly with a diene as termonomer, in the presence of a Ziegler-Natta catalyst including an aluminium trialkyl and a solid component of catalyst containing titanium, magnesium, chlorine and alkoxy groups, said solid component of catalyst being prepared according to the following procedure:

- (i) a solid support and granular $MgCl_2$, obtained by spray drying an alcohol solution of $MgCl_2$ and having an alcohol hydroxyl content of 18 to 25% by weight, expressed as a weight of ethanol, is suspended in a liquid hydrocarbon solvent and an aliphatic alcohol R' -OH, wherein R' is an alkyl radical, linear or branched, containing from 1 to 5 carbon atoms, and a titanium tetra-alkoxide $Ti(OR)_4$, wherein R is an alkyl radical, linear or branched, containing from 1 to 8 carbon atoms, are added to the suspension thus obtained, with a molar ratio R' -OH/ $MgCl_2$ of 0.5:1 to 1.5:1 and with a molar ratio $MgCl_2/Ti(OR)_4$ of 0.3:1 to 3:1;
- (ii) the suspension of step (i) is heated until a homogeneous solution is obtained and the solution is cooled to precipitate a granular solid;
- (iii) the granular solid obtained in step (ii), in the relative suspension, is put in contact and interacted with an alkyl aluminium chloride having the formula $AIR''_nCl_{(3-n)}$, wherein R'' is an alkyl radical, linear or branched, containing from 1 to 20 carbon atoms, with a ratio between the chlorine atoms, in said aluminium chloride, and the total alkoxy groups of 0.4:1 to 1.2:1;
- (iv) the solid component of catalyst is recovered from the reaction products of step (iii).

With respect to the preparation of the solid component of catalyst, the support of magnesium chloride, used in step (i) of the procedure, can be prepared according to the method known in the art, by dissolving anhydrous or basically

anhydrous magnesium chloride in ethanol, and spray-drying the solution in a spray-drying apparatus. In particular the solution is sprayed with a nozzle or other equivalent device, in the evaporation chamber of a spray-drier and the liquid particles thus formed are put in contact with a flow of inert gas fed into the evaporation chamber in countercurrent or equicurrent. The procedure is usually carried out with a temperature of the gaseous flow at the inlet of about 250-400°C, 5 with a temperature of the gaseous flow at the outlet of 140-250°C and with a difference of temperature between the flows at the inlet and outlet of at least 40°C. Under these conditions it is possible to recover from the drier a solid in the form of particles, with an apparent density of 0.30-0.46 g/ml, a particle size of 1-100 µm (average size 10-20 µm), a surface area of 12-17 m²/g, total porosity of 65-85 volume % and content of alcohol hydroxyls of 18 to 25% by weight expressed as a weight of ethanol.

10 The support of magnesium chloride thus prepared is suspended in a liquid hydrocarbon solvent, for example, hexane, pentane, decane or dodecane, and a titanium tetra-alkoxide, which can be selected for example from titanium tetra n-propoxide, titanium tetra n-butoxide, titanium tetra i-propoxide and titanium tetra i-butoxide, is added to the solution thus obtained. The preferred compound is titanium tetra n-butoxide. An aliphatic alcohol, for example methanol, ethanol, propanol, isopropanol, n-butanol and n-pentanol, is also added to the suspension. The preferred aliphatic 15 alcohol is n-butanol. In the preferred method the molar ratio R'-OH/MgCl₂ is 1.5:1 and the molar ratio MgCl₂/Ti(OR)₄ is 1:1.

10 The suspension thus obtained is heated in step (ii) normally to temperatures of 80-100°C, until a homogeneous solution is obtained and this solution is cooled, preferably gradually, to room temperature (20-25°C) or to a value close 20 to room temperature to cause the formation of a solid precipitate. This precipitate is typically in granule form with a size generally ranging from 10 to 100 µm (average size 30-45 µm), with an apparent density of 0.45 to 0.50 g/ml, a surface area of 7-10 m²/g, porosity of 55-70 volume % and a content of alcohol hydroxyls of 60-65% by weight as R'-OH alcohol and 1-5% by weight as ethanol. It has been found that the alcohol is practically absent in the liquid phase of the suspension, the concentration being at values of a few parts per million.

25 An alkyl aluminium chloride, normally selected from aluminium diethyl monochloride, aluminium ethyl dichloride and aluminium ethyl sesquichloride, is added to the suspension obtained in step (ii), and the mixture is normally kept at a temperature ranging from room temperature (20-25°C) to 80°C, for a period of 30 to 120 minutes. In the preferred method in step (iii) the ratio between the chlorine atoms, in said alkyl aluminium chloride, and the total alkoxy groups is 0.65:1, the alkyl aluminium chloride, possibly diluted in a hydrocarbon solvent, is added to the suspension which is kept at a temperature of 30-35°C and the resulting suspension is then heated to 60°C for 1 hour.

30 The solid component of catalyst is finally recovered from the reaction products of step (III), for example by filtration or decanting and is washed with a hydrocarbon solvent and possibly dried.

35 The solid component of catalyst thus obtained is a spherical granular solid, with a granule size generally ranging from 1 to 30 µm (average size 7-15 µm), a surface area of 10-20 m²/g, porosity of 65-85 volume %, apparent density of 0.4-0.5 g/ml, and with the following composition expressed in atomic proportions:



wherein R' is an alkyl radical, linear or branched, containing from 1 to 5 carbon atoms and preferably n-butyl.

40 The titanium present in the solid component of catalyst is partly in a trivalent form and partly in a tetravalent form with a ratio between trivalent titanium and the total titanium of 0.6:1 to 1:1.

The catalyst used in the process of the present invention includes the solid component of catalyst described above and an aluminium trialkyl, especially an aluminium trialkyl wherein the alkyl contains from 2 to 6 carbon atoms. The preferred aluminium trialkyl is aluminium tributyl. An atomic ratio between the aluminium and titanium of 5:1 to 400:1 45 is normally kept in the catalyst.

The α-olefins which can be used in the process of the present invention generally contain from 3 to 8 carbon atoms. Among these propylene and butene-1 are preferred. Propylene is particularly preferred.

Apart from ethylene/α-olefin copolymers, the process of the present invention can also be used to prepare ethylene/50 α-olefin/diene terpolymers, also having elastomeric properties. For this purpose, conjugated or non-conjugated dienes can be used as comonomers, of the cyclic or acyclic type, generally having from 4 to 12 carbon atoms, such as, for example, 5-ethylidene-2-norbornene, trans-1,4-hexadiene, 1,3-butadiene, etc. The content of terpolymer in the diene generally ranges from 1 to 20% by weight, preferably from 2 to 6% by weight.

The process is carried out in suspension, in a reaction medium in which the polymer produced is basically insoluble. The reaction medium is preferably prevalently composed of one of the comonomers, to which a saturated hydrocarbon 55 is added as a diluent, or a mixture of different saturated hydrocarbons, in liquid form under the reaction conditions, having from 2 to 5 carbon atoms, such as ethane, propane, butane.

The polymerization temperature is normally kept, according to the process of the present invention, from 0 to 60°C, preferably from 25 to 55°C. The contact times normally vary from 15 minutes to 4 hours, preferably from 30 minutes

to 1 hour. The polymerization is generally carried out in the presence of hydrogen as a molecular weight moderator and regulator, operating under a total pressure ranging from 5 to 50 bar, preferably from 8 to 30 bar, with a ratio between the ethylene pressure and the hydrogen pressure higher than 4 and preferably higher than 20.

The elastomeric copolymers obtained according to the process of the present invention generally contain from 35 to 85% by weight, preferably from 45 to 75% by weight, of ethylene.

The process of the present invention produces elastomeric copolymers of ethylene with α -olefins, as well as ethylene/ α -olefin/diene terpolymers, having a low crystallinity even with a high content of linked ethylene. In fact a 3% crystallinity has been observed for copolymers with about 68% by weight of linked ethylene, which is considered as traces for copolymers having about 59% by weight of ethylene.

The process of the present invention is also characterized by particularly high productivity and yields compared to those of similar processes of the known art.

These and other advantages arising from the present invention will be better illustrated by the examples which follow which, however, do not limit the invention in any way.

The "crude" copolymers were characterized with the following parameters:

- COMPOSITION AND PRODUCT OF THE REACTIVITY RATIOS OF THE COMONOMERS $r_1 \cdot r_2$: were determined by infra-red analysis. In particular the quantity of propylene is calculated on the basis of the ratio between the absorption intensities at 4390 and 4255 cm^{-1} ; the product $r_1 \cdot r_2$ is determined on the basis of absorptions at 973 and 935 cm^{-1} .
- MOLECULAR WEIGHT DISTRIBUTION (RATIO M_w/M_n): was determined by gel permeation chromatography, in 1,2-dichlorobenzene at 135°C, using 4 columns in series containing, as a stationary phase, PL-GEL^(R) (cross-linked styrene-divinylbenzene resin, produced by POLYMER LAB) with particles of 10 μm and porosity respectively 10², 10³, 10⁴, 10⁵ nm. The calculation of molecular weights was corrected in relation to the average composition of the copolymer according to the equation proposed by Sholte.
- MOONEY ML(1+4) VISCOSITY: was determined at 100 and 125°C both on the "crude" polymer and in mixture, according to the ASTM D1646-87 method.

The mixtures for vulcanization were prepared in an open mixer, with the following composition:

- | | |
|----|--|
| 30 | 100 p/p of copolymer |
| | 5 p/p of zinc oxide |
| | 55 p/p of FEF carbon black |
| | 30 p/p of branched polyalkylbenzene oil |
| | 0.37 p/p of sulphur |
| 35 | 5 p/p of Peroximon ^(R) F-40 (1,3-bis-(terbutyl-peroxiisopropyl)-benzene). |

The vulcanization was carried out in a plate press at 165°C for 40'. The traction tests (ultimate tensile strength and elongation to break) and the determination of the tension set of the vulcanized products were carried out in accordance with the method ASTM D412-87.

40 The X-ray crystallinity was determined using a diffractometer for powders.

EXAMPLE 1

Preparation of the solid component of catalyst.

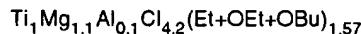
- 45 (i) An ethanol solution of magnesium chloride is spraydried to prepare a solid support of catalyst in the form of spherical particles, with a particle size of 3 to 100 μm (average size 15 μm), having an apparent density of 0.30 g/ml, a surface area of 17 m^2/g , a porosity of 75 volume %, and a content of alcohol hydroxyls of 22% by weight (expressed as ethanol). 2.45 g of this support are suspended in 50 ml of anhydrous n-decane in a 250 ml reactor, under stirring. 2.8 ml of n-butanol and 7 g of titanium tetra-n-butoxide are added to the suspension.
- 50 (ii) The suspension is heated to 100°C for 60 minutes, operating under nitrogen. A limpid solution is obtained which is cooled to room temperature (20-25°C), with the precipitation of an inflated solid in the form of spherical particles, having a particle size of 10 to 100 μm (average size 35 μm), an apparent density of 0.5 g/ml, a surface area of 8 m^2/g , porosity of 65 volume %, and content of alcohol hydroxyls of 60% by weight (expressed as butanol).
- 55 (iii) 19.7 g of aluminium ethyl sesquichloride dissolved in 50 ml of n-decane (ratio between the chlorine atoms of the aluminium ethyl sesquichloride and the total alkoxy groups ($\text{OEt}+\text{OBu}$) = 0.65:1), are added dropwise to the suspension kept under stirring and at a temperature of 35°C. At the end of the addition the suspension is heated for 1 hour to 60°C.

(iv) The solid is filtered on a porous glass septum. 8 g of a solid component of catalyst are thus obtained, which are washed with 3 100 ml portions of n-decane.

The solid component of catalyst thus obtained has the following characteristics:

- 5 - titanium content: 13.4% by weight, with a ratio between the titanium in its trivalent state and the total titanium (trivalent plus tetravalent) of 0.80:1;
- magnesium content: 7.7% by weight;
- aluminium content: 1.0% by weight;
- 10 - chlorine content: 42.4% by weight;
- content of organic fraction: 35.5% by weight; the organic fraction is basically composed of ethyl groups (Et), ethoxy groups (OEt) and n-butoxy groups (OBu).

Expressing the components according to their atomic proportions, the component of catalyst can be represented by the formula:



20 wherein OEt represents 3.7% and OBu 30.8% by weight of the total.

Copolymerization of ethylene with propylene.

440 g of liquid propylene are placed in a 1.7 dm³ perfectly anhydrous cylindrical autoclave equipped with a stirrer.

25 The temperature of the autoclave is regulated at 50°C. It is then saturated with ethylene until an excess pressure of 4.5 bar is reached and then an excess pressure of 1.2 bar of hydrogen is added. The total pressure on the head of the autoclave is 25.0 bar.

30 7.4 mg of the solid component of catalyst prepared as described above and 5 mmoles of aluminium tributyl dissolved in 25 cm³ of anhydrous hexane are then introduced contemporaneously. The reaction is carried out at a constant temperature, and the ethylene fed continuously to keep the total pressure constant.

After one hour from the beginning of the reaction 142 g of copolymer are recovered, equal to a yield of 143200 g of product per g of titanium per hour.

The characteristics of the "crude" and vulcanized copolymer, prepared as described above, are shown in Table I.

EXAMPLE 2

445 g of liquid propylene are charged into a 1.7 dm³ perfectly anhydrous cylindrical autoclave equipped with a stirrer. The thermostat of the autoclave is fixed at 40°C. It is then saturated with ethylene until an excess pressure of 4 bar is reached and then an excess pressure of 0.3 bar of hydrogen is added. The total pressure on the head of the 40 autoclave is 19.8 bar.

12 mg of the solid component of catalyst prepared as described in Example 1 and 5 mmoles of aluminium tributyl dissolved in 25 cm³ of anhydrous hexane are then introduced contemporaneously. The reaction is carried out using the same procedure as described in Example 1.

45 After an hour from the beginning of the reaction 160 g of copolymer are recovered, equal to a yield of 99500 g of product per g of titanium per hour.

The characteristics of the "crude" and vulcanized copolymer, prepared as described above, are shown in Table I.

EXAMPLE 3

50 450 g of liquid propylene are charged into a 1.7 dm³ perfectly anhydrous cylindrical autoclave equipped with a stirrer. The thermostat of the autoclave is regulated at 50°C. It is then saturated with ethylene until an excess pressure of 3.3 bar is reached and an excess pressure of 0.3 bar of hydrogen is then added. The total pressure on the head of the autoclave is 22.9 bar.

55 10.7 mg of the solid component of catalyst prepared as described in Example 1 and 5 mmoles of aluminium tributyl dissolved in 25 cm³ of anhydrous hexane are introduced contemporaneously. The reaction is carried out using the same procedure as described in Example 1.

After an hour from the beginning of the reaction 134 g of copolymer are recovered, equal to a yield of 93500 g of product per g of titanium per hour.

EP 0 544 340 B1

The characteristics of the "crude" and vulcanized copolymer, prepared as described above, are shown in Table I.

EXAMPLE 4

5 465 g of liquid propylene are charged into a 1.7 dm³ perfectly anhydrous cylindrical autoclave equipped with a stirrer. The thermostat of the autoclave is regulated at 40°C. It is then saturated with ethylene until an excess pressure of 2.5 bar is reached and then an excess pressure of 0.3 bar of hydrogen is added. The total pressure on the head of the autoclave is 18.2 bar.

10 15.4 mg of the solid component of catalyst prepared as described in Example 1 and 5 mmoles of aluminium tributyl dissolved in 25 cm³ of anhydrous hexane are then introduced contemporaneously. The reaction is carried out using the same procedure described in Example 1.

After an hour from the beginning of the reaction 134 g of copolymer are recovered, equal to a yield of 93500 g of product per g of titanium per hour.

The characteristics of the "crude" and vulcanized copolymer, prepared as described above, are shown in Table I.

15

EXAMPLE 5

20 840 g of liquid propylene are charged into a 2.8 dm³ perfectly anhydrous cylindrical autoclave equipped with a stirrer. The thermostat of the autoclave is regulated at 40°C. It is then saturated with ethylene until an excess pressure of 2.0 bar is reached and then an excess pressure of 0.3 bar of hydrogen is added. The total pressure on the head of the autoclave is 17.5 bar.

25 21.4 mg of the solid component of catalyst prepared as described in Example 1 and 5 mmoles of aluminium tributyl dissolved in 25 cm³ of anhydrous hexane are then introduced contemporaneously. The reaction is carried out using the same procedure described in Example 1.

25 After an hour from the beginning of the reaction 193 g of the copolymer are recovered, equal to a yield of 67300 g of product per g of titanium per hour.

The characteristics of the "crude" and vulcanized copolymer, prepared as described above, are described in Table I.

30

30 450 g of liquid propylene are charged into a 1.7 dm³ perfectly anhydrous cylindrical autoclave equipped with a stirrer. The thermostat of the autoclave is regulated at 40°C. It is then saturated with ethylene until an excess pressure of 3.0 bar is reached and an excess pressure of 0.3 bar of hydrogen are then added. The total pressure on the head of the autoclave is 18.7 bar.

35 12.9 mg of the solid component of catalyst prepared as described in Example 1 and 5 mmoles of aluminium tributyl dissolved in 25 cm³ of anhydrous hexane are then introduced contemporaneously. The reaction is carried out using the same procedure as described in Example 1.

35 After an hour from the beginning of the reaction 200 g of copolymer are recovered, equal to a yield of 115700 g of product per g of titanium per hour.

40

40 The characteristics of "crude" and vulcanized copolymer, prepared as described above, are shown in Table I.

45

50

55

TABLE I

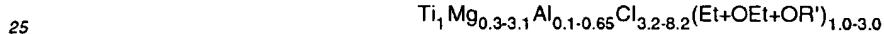
Ex.	Crude copolymer				Mixt.	Vulcaniz. polymer			Tens. Set 200%	
	Composition C ₂ H ₄ (w/w%)	C ₃ H ₆ (w/w%)	r ₁ *r ₂	Intrin. viscos. (dl/g)		Mw/ Mn	ML1+4 100°C	ML1+4 125°C	Cry sta (\$)	
1	70.3	29.7	2.94	1.7	5.1	52	33	--	41	150
2	67.6	32.4	2.83	1.7	3.9	--	53.5	3	64	175
3	65.8	34.2	4.11	1.93	6.2	61	46.5	--	49.5	154
4	59.3	40.7	3.67	1.54	6.9	48	--	tra ces	42	149
5	57.6	42.4	4.11	1.66	--	58.5	39	--	36.5	101
6	56.8	43.2	>5	0.92	--	22.5	18.5	--	18.5	89

5
10
15
20
25
30
35
40
45
50
55

Claims

1. Process for the preparation of elastomeric copolymers of ethylene, wherein ethylene is copolymerized with an α -olefin, and possibly with a diene as termonomer, in the presence of a Ziegler-Natta catalyst including an aluminium trialkyl and a solid component of catalyst containing titanium, magnesium, aluminium, chlorine and alkoxy groups, said solid component of catalyst being prepared according to the following procedure:
 - (i) a solid, granular support of $MgCl_2$, obtained by spray-drying an alcohol solution of $MgCl_2$ and having a content of alcohol hydroxyls of 18 to 25% by weight, expressed as a weight of ethanol, is suspended in a liquid hydrocarbon solvent and an aliphatic alcohol $R'-OH$, wherein R' is a linear or branched alkyl radical, containing from 1 to 5 carbon atoms, is added to the suspension thus obtained, together with a titanium tetra-alkoxide $Ti(OR)_4$, wherein R is a linear or branched alkyl radical, containing from 1 to 8 carbon atoms, with a molar ratio $R'-OH/MgCl_2$ of 0.5:1 to 1.5:1 and a molar ratio $MgCl_2/Ti(OR)_4$ of 0.3:1 to 3:1;
 - (ii) the suspension of step (i) is heated until a homogeneous solution is obtained and the solution is cooled to precipitate a granular solid;
 - (iii) the granular solid obtained in step (ii), in the relative suspension, is put in contact and interacted with an alkyl aluminium chloride having the formula $AIR''_nCl_{(3-n)}$, wherein R'' is a linear or branched alkyl radical, containing from 1 to 20 carbon atoms, with a ratio between the chlorine atoms, in said aluminium chloride, and the total alkoxy groups of 0.4:1 to 1.2:1;
 - (iv) the solid component of catalyst is recovered from the reaction products of step (iii).
2. Process according to Claim 1, wherein the α -olefin contains from 3 to 8 carbon atoms.
3. Process according to Claim 2, wherein the α -olefin is propylene.
4. Process according to Claim 2, wherein the α -olefin is butene-1.
5. Process according to any of the previous Claims, wherein the diene possibly used as termonomer contains from 4 to 12 carbon atoms.
6. Process according to Claim 5, wherein the diene is selected from 5-ethylidene-2-norbornene, trans-1,4-hexadiene and 1,3-butadiene.
7. Process according to any of the previous Claims, wherein the polymerization is carried out in suspension, in a reaction medium prevalently composed of one of the comonomers, to which a saturated hydrocarbon is added as diluent, or a mixture of different saturated hydrocarbons, liquid under the reaction conditions, having from 2 to 5 carbon atoms.
8. Process according to any of the previous Claims, wherein the polymerization temperature is kept within a range of 0°C to 60°C.
9. Process according to Claim 8, wherein the polymerization temperature is kept within a range of 25°C to 55°C.
10. Process according to any of the previous Claims, wherein the polymerization is carried out in the presence of hydrogen as a molecular weight moderator and regulator, operating under a total pressure of 5 to 50 bar, with a ratio between the ethylene pressure and the hydrogen pressure higher than 4.
11. Process according to any of the previous Claims, wherein the support of magnesium chloride, used in step (i), has an apparent density of 0.30-0.46 g/ml, a granule size of 1-100 μm (average size 10-20 μm), a surface area of 12-17 m^2/g , a total porosity of 65-85 volume %.
12. Process according to any of the previous Claims, wherein the titanium tetra-alkoxide used in step (i) is selected from titanium tetra n-propoxide, titanium tetra n-butoxide, titanium tetra i-propoxide and titanium tetra i-butoxide.
13. Process according to Claim 12, wherein the titanium tetra-alkoxide is titanium tetra n-butoxide.
14. Process according to any of the previous Claims, wherein the aliphatic alcohol $R'-OH$ used in step (i) is selected from methanol, ethanol, propanol, isopropanol, n-butanol and n-pentanol.

15. Process according to Claim 14, wherein the aliphatic alcohol R'-OH is n-butanol.
16. Process according to any of the previous Claims, wherein in step (i) a molar ratio R'-OH/MgCl₂ of 1.5:1 and a molar ratio MgCl₂/Ti(OR)₄ of 1:1 are used.
- 5 17. Process according to any of the previous Claims, wherein the granular solid obtained in step (ii) is composed of granules having a size ranging from 10 to 100 µm (average size 30-45 µm), an apparent density of 0.45 to 0.50 g/ml, a surface area of 7-10 m²/g, a porosity of 55-70 volume % and with a content of alcohol hydroxyls of 60-65% by weight as R'-OH alcohol and 1-5% by weight as ethanol.
- 10 18. Process according to any of the previous Claims, wherein in step (iii), the alkyl aluminium chloride is selected from aluminium diethyl monochloride, aluminium ethyl dichloride and aluminium ethyl sesquichloride and the procedure is carried out at a temperature ranging from room temperature to 80°C, for a period ranging from 30 to 120 minutes.
- 15 19. Process according to any of the previous Claims, wherein in step (iii) the ratio between the chlorine atoms, in said alkyl aluminium chloride, and the total alkoxy groups is 0.65:1, the alkyl aluminium chloride, possibly diluted in a hydrocarbon solvent, is added to the suspension kept at a temperature of 30-35°C and the resulting suspension is then heated to 60°C for 1 hour.
- 20 20. Process according to any of the previous Claims, wherein the solid component of catalyst is a spherical granular solid, with a granule size of 1 to 30 µm (average size 7-15 µm), a surface area of 10-20 m²/g, a porosity of 65-85 volume %, an apparent density of 0.4-0.5 g/ml, and with the following composition expressed in atomic proportions:



wherein R' is a linear or branched alkyl radical, containing from 1 to 5 carbon atoms and the titanium is partly in a trivalent form and partly in a tetravalent form, with a ratio between the trivalent titanium and the total titanium of 0.6:1 to 1:1.

- 30 21. Process according to any of the previous Claims, wherein an atomic ratio between the aluminium and the titanium of 5:1 to 400:1 is maintained in the Ziegler-Natta catalyst.
22. Process according to any of the previous Claims, wherein the alkyl of the aluminium trialkyl contains from 2 to 6 carbon atoms.
- 35 23. Process according to Claim 22, wherein the aluminium trialkyl is aluminium tributyl.

40 Patentansprüche

1. Verfahren zur Herstellung von elastomeren Ethylen-Copolymeren, worin Ethylen mit einem α-Olefin und gegebenenfalls mit einem Dien als Termonomer in Gegenwart eines Ziegler-Natta-Katalysators, welcher Aluminiumtrialkyl und einen festen Katalysatorbestandteil, enthaltend Titan, Magnesium, Aluminium, Chlor und Alkoxygruppen, einschließt, copolymerisiert wird, wobei der feste Katalysatorbestandteil nach der folgenden Arbeitsweise hergestellt wird:
- 45 (i) ein fester körniger MgCl₂-Träger, welcher durch Sprührocknen einer alkoholischen MgCl₂-Lösung erhalten wird und einen Gehalt an alkoholischen Hydroxylen von 18 bis 25 Gew.% aufweist, ausgedrückt als Gewicht von Ethanol, wird in einem flüssigen Kohlenwasserstoff-Lösungsmittel suspendiert, und ein aliphatischer Alkohol R'-OH, worin R' eine gerade oder verzweigte Alkylgruppe mit 1 bis 5 Kohlenstoffatomen ist, wird zusammen mit einem Titan-tetraalkoxid Ti(OR)₄, worin R eine gerade oder verzweigte Alkylgruppe mit 1 bis 8 Kohlenstoffatomen ist, zu der so erhaltenen Suspension gegeben, wobei das Molverhältnis von R'-OH/MgCl₂ 0,5:1 bis 1,5:1 und das Molverhältnis von MgCl₂/Ti(OR)₄ 0,3:1 bis 3:1 beträgt;
- 50 (ii) die Suspension aus Schritt (i) wird erhitzt, bis eine homogene Lösung erhalten wird, und die Lösung wird zur Ausfällung eines körnigen Feststoffs abgekühlt;
- 55 (iii) der in Schritt (ii) erhaltene körnige Feststoff wird in der entsprechenden Suspension mit einem Alkylaluminiumchlorid der Formel AlRⁿCl_(3-n), worin Rⁿ eine gerade oder verzweigte Alkylgruppe mit 1 bis 20 Koh-

EP 0 544 340 B1

lenstoffatomen ist, in Kontakt und Wechselwirkung gebracht, wobei das Verhältnis zwischen den Chloratomen im Aluminiumchlorid und den Gesamt-Alkoxygruppen 0,4:1 bis 1,2:1 beträgt;
(iv) der feste Katalysatorbestandteil wird aus den Reaktionsprodukten von Schritt (iii) gewonnen.

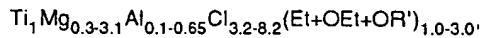
- 5 2. Verfahren nach Anspruch 1, worin das α -Olefin 3 bis 8 Kohlenstoffatome enthält.
- 10 3. Verfahren nach Anspruch 2, worin das α -Olefin Propylen ist.
- 15 4. Verfahren nach Anspruch 2, worin das α -Olefin But-1-en ist.
- 20 5. Verfahren nach einem der vorhergehenden Ansprüche, worin das gegebenenfalls als Termonomer verwendete Dien 4 bis 12 Kohlenstoffatome enthält.
- 25 6. Verfahren nach Anspruch 5, worin das Dien ausgewählt ist aus 5-Ethyliden-2-norbornen, Trans-1,4-hexadien und 1,3-Butadien.
- 30 7. Verfahren nach einem der vorhergehenden Ansprüche, worin die Polymerisation in Suspension in einem Reaktionsmedium ausgeführt wird, welches in erster Linie aus einem der Comonomere gebildet ist, die mit einem gesättigten Kohlenwasserstoff als Verdünnungsmittel oder einer unter den Reaktionsbedingungen flüssigen Mischung von verschiedenen gesättigten Kohlenwasserstoffen mit 2 bis 5 Kohlenstoffatomen, versetzt werden.
- 35 8. Verfahren nach einem der vorhergehenden Ansprüche, worin die Polymerisationstemperatur in einem Bereich von 0°C bis 60°C gehalten wird.
- 40 9. Verfahren nach Anspruch 8, worin die Polymerisationstemperatur in einem Bereich von 25°C bis 55°C gehalten wird.
- 45 10. Verfahren nach einem der vorhergehenden Ansprüche, worin die Polymerisation in Gegenwart von Wasserstoff als Molekulargewichtsmoderator und -regulator durchgeführt wird, wobei unter einem Gesamtdruck von 5 bis 50 bar bei einem Verhältnis zwischen Ethyldruck und Wasserstoffdruck von über 4 gearbeitet wird.
- 50 11. Verfahren nach einem der vorhergehenden Ansprüche, worin der in Schritt (i) verwendete Träger aus Magnesiumchlorid eine Fülldichte von 0,30-0,46 g/ml, eine Körnchengröße von 1-100 µm (durchschnittliche Größe 10-20 µm), eine Oberfläche von 12-17 m²/g und eine Gesamtporosität von 65-85 Vol.% aufweist.
- 55 12. Verfahren nach einem der vorhergehenden Ansprüche, worin das in Schritt (i) verwendete Titantetraalkoxid ausgewählt ist aus Titantetra-n-propoxid, Titantetra-n-butoxid, Titantetra-i-propoxid und Titantetra-i-butoxid.
- 60 13. Verfahren nach Anspruch 12, worin das Titantetraalkoxid Titantetra-n-butoxid ist.
- 65 14. Verfahren nach einem der vorhergehenden Ansprüche, worin der in Schritt (i) verwendete aliphatische Alkohol R'-OH ausgewählt ist aus Methanol, Ethanol, Propanol, Isopropanol, n-Butanol und n-Pentanol.
- 70 15. Verfahren nach Anspruch 14, worin der aliphatische Alkohol R'-OH n-Butanol ist.
- 75 16. Verfahren nach einem der vorhergehenden Ansprüche, worin in Schritt (i) ein Molverhältnis R'-OH/MgCl₂ von 1,5:1 und ein Molverhältnis MgCl₂/Ti(OR)₄ von 1:1 verwendet wird.
- 80 17. Verfahren nach einem der vorhergehenden Ansprüche, worin der in Schritt (ii) erhaltene körnige Feststoff aus Körnchen mit einer Größe im Bereich von 10 bis 100 µm (durchschnittliche Größe 30-45 µm), einer Fülldichte von 0,45 bis 0,50 g/ml, einer Oberfläche von 7-10 m²/g, einer Porosität von 55-70 Vol.% und einem Gehalt an alkoholischen Hydroxylen von 60-65 Gew.% als R'-OH-Alkohol und 1-5 Gew.% als Ethanol gebildet ist.
- 85 18. Verfahren nach einem der vorhergehenden Ansprüche, worin in Schritt (iii) das Alkylaluminiumchlorid ausgewählt ist aus Aluminiumdiethylmonochlorid, Aluminiummethyldichlorid und Aluminiummethylesquichlorid und das Verfahren bei einer Temperatur im Bereich von Raumtemperatur bis 80°C über einen Zeitraum von 30 bis 120 Minuten durchgeführt wird.

19. Verfahren nach einem der vorhergehenden Ansprüche, worin in Schritt (iii) das Verhältnis zwischen Chloratomen im Alkylaluminiumchlorid und den Gesamt-Alkoxygruppen 0,65:1 beträgt, das gegebenenfalls in einem Kohlenwasserstoff-Lösungsmittel verdünnte Alkylaluminiumchlorid zu der auf einer Temperatur von 30-35°C gehaltenen Suspension gegeben wird und die resultierende Suspension dann 1 Stunde lang auf 60°C erhitzt wird.

5

20. Verfahren nach einem der vorhergehenden Ansprüche, worin der feste Katalysatorbestandteil ein kugelförmiger körniger Feststoff mit einer Körnungsröße von 1 bis 30 µm (durchschnittliche Größe 7-15 µm), einer Oberfläche von 10-20 m²/g, einer Porosität von 65-85 Vol.-%, einer Fülldichte von 0,4 bis 0,5 g/ml und mit der folgenden Zusammensetzung, ausgedrückt in atomaren Verhältnissen:

10



15 ist, worin R' eine gerade oder verzweigte Alkylgruppe mit 1 bis 5 Kohlenstoffatomen ist und das Titan zum Teil in trivalenter Form und zum Teil in tetravalenter Form vorliegt, wobei das Verhältnis zwischen trivalentem Titan und Gesamt-Titan 0,6:1 bis 1:1 beträgt.

21. Verfahren nach einem der vorhergehenden Ansprüche, worin ein atomares Verhältnis zwischen Aluminium und Titan von 5:1 bis 400:1 im Ziegler-Natta-Katalysator aufrechtgehalten wird.

20

22. Verfahren nach einem der vorhergehenden Ansprüche, worin das Alkyl des Aluminiumtrialkyls 2 bis 6 Kohlenstoffatome enthält.

25

23. Verfahren nach Anspruch 22, worin das Aluminiumtrialkyl Aluminiumtributyl ist.

Revendications

1. Procédé de préparation de copolymères élastomères de l'éthylène, dans lequel on fait copolymériser de l'éthylène avec une α-oléfine et, éventuellement, un termonomère diénique, en présence d'un catalyseur de type Ziegler-Natta comportant un trialkyl-aluminium et un composant solide de catalyseur qui contient du titane, du magnésium, de l'aluminium, du chlore et des groupes alcoxy, ce composant solide de catalyseur étant préparé selon le protocole suivant :

35

a) on met un support solide granulaire à base de MgCl₂, obtenu par dessiccation par pulvérisation d'une solution de MgCl₂ dans de l'alcool et contenant de 18 à 25 % en poids de groupes hydroxy alcooliques (teneur exprimée en poids d'éthanol), en suspension dans un solvant de type hydrocarbure liquide, et l'on ajoute à la suspension ainsi obtenue un alcool aliphatique de formule R'-OH, dans laquelle R' représente un groupe alkyle linéaire ou ramifié comportant de 1 à 5 atomes de carbone, conjointement avec un tétra-alcoxy-titane de formule Ti(OR)₄, dans laquelle R représente un groupe alkyle linéaire ou ramifié comportant de 1 à 8 atomes de carbone, en un rapport molaire R'-OH/MgCl₂ de 0,5/1 à 1,5/1 et un rapport molaire MgCl₂/Ti(OR)₄ de 0,3/1 à 3/1 ;

40

b) on chauffe la suspension obtenue lors de l'étape (a) jusqu'à ce qu'on obtienne une solution homogène, et l'on refroidit cette solution pour faire précipiter un solide granulaire ;

45

c) on met ce solide granulaire obtenu lors de l'étape (b), qui se trouve en suspension, en contact et en interaction avec un chlorure d'alkyl-aluminium de formule AlRⁿCl_(3-n), dans laquelle Rⁿ représente un groupe alkyle linéaire ou ramifié comportant de 1 à 20 atomes de carbone, en un rapport de 0,4/1 à 1,2/1 entre le nombre d'atomes de chlore présents dans ledit chlorure d'alkyl-aluminium et le nombre total de groupes alcoxy ;

50

d) on récupère, dans les produits de la réaction de l'étape (c), le composant solide de catalyseur.

2. Procédé conforme à la revendication 1, dans lequel l'α-oléfine comporte de 3 à 8 atomes de carbone.

55

3. Procédé conforme à la revendication 2, dans lequel l'α-oléfine est du propylène.

4. Procédé conforme à la revendication 2, dans lequel l'α-oléfine est du butène-1.

5. Procédé conforme à l'une des revendications précédentes, dans lequel le diène éventuellement employé comme

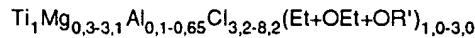
termonomère comporte de 4 à 12 atomes de carbone.

6. Procédé conforme à la revendication 5, dans lequel le diène est choisi parmi le 5-éthylidène-2-norbornène, le trans-1,4-hexadiène et le 1,3-butadiène.
7. Procédé conforme à l'une des revendications précédentes, dans lequel on réalise la polymérisation en suspension, dans un milieu réactionnel principalement constitué de l'un des comonomères, auquel est ajouté, en tant que diluant, un hydrocarbure saturé ou un mélange de divers hydrocarbures saturés, comportant de 2 à 5 atomes de carbone, qui est liquide dans les conditions de la réaction.
8. Procédé conforme à l'une des revendications précédentes, dans lequel la température de polymérisation est maintenue dans l'intervalle allant de 0°C à 60°C.
9. Procédé conforme à la revendication 8, dans lequel la température de polymérisation est maintenue dans l'intervalle allant de 25°C à 55°C.
10. Procédé conforme à l'une des revendications précédentes, dans lequel on réalise la polymérisation en présence d'hydrogène, employé comme agent de modération et d'ajustement de la masse moléculaire, en opérant sous une pression totale de 5 à 50 bar et avec un rapport supérieur à 4 entre la pression d'éthylène et la pression d'hydrogène.
11. Procédé conforme à l'une des revendications précédentes, dans lequel le support à base de chlorure de magnésium, employé dans l'étape (a), possède une masse volumique apparente de 0,30 à 0,46 g/ml, comporte des granules dont la taille va de 1 à 100 µm et dont la taille moyenne vaut de 10 à 20 µm, et présente une aire spécifique de 12 à 17 m²/g et une porosité totale de 65 à 85 % en volume.
12. Procédé conforme à l'une des revendications précédentes, dans lequel le tétra-alcoxy-titanate utilisé dans l'étape (a) est choisi parmi le tétra-n-propoxy-titanate, le tétra-n-butoxy-titanate, le tétra-i-propoxy-titanate et le tétra-i-butoxy-titanate,
13. Procédé conforme à la revendication 12, dans lequel le tétra-alcoxy-titanate est du tétra-n-butoxy-titanate.
14. Procédé conforme à l'une des revendications précédentes, dans lequel l'alcool aliphatique R'-OH utilisé dans l'étape (a) est choisi parmi le méthanol, l'éthanol, le propanol, l'isopropanol, le n-butanol et le n-pentanol.
15. Procédé conforme à la revendication 14, dans lequel l'alcool aliphatique R'-OH est du n-butanol.
16. Procédé conforme à l'une des revendications précédentes, dans lequel, au cours de l'étape (a), le rapport molaire R'-OH/MgCl₂ vaut 1,5/1 et le rapport molaire MgCl₂/Ti(OR)₄ vaut 1/1.
17. Procédé conforme à l'une des revendications précédentes, dans lequel le solide granulaire obtenu dans l'étape (b) est constitué de granules dont la taille va de 10 à 100 µm et dont la taille moyenne vaut de 30 à 45 µm, et présente une masse volumique apparente de 0,45 à 0,50 g/ml, une aire spécifique de 7 à 10 m²/g et une porosité de 55 à 70 % en volume, ainsi qu'une teneur en groupes hydroxy alcooliques de 60 à 65 % en poids, exprimée en alcool R'-OH, et de 1 à 5 % en poids, exprimée en éthanol.
18. Procédé conforme à l'une des revendications précédentes, dans lequel le chlorure d'alkyl-aluminium employé dans l'étape (c) est choisi parmi le monochlorure de diéthyl-aluminium, le dichlorure d'éthyl-aluminium et le sesquichlorure d'éthyl-aluminium, cette étape du protocole étant mise en oeuvre à une température située dans l'intervalle allant de la température ambiante à 80°C et pendant un laps de temps de 30 à 120 minutes.
19. Procédé conforme à l'une des revendications précédentes, dans lequel, dans l'étape (c), le rapport entre le nombre d'atomes de chlore présents dans le chlorure d'alkyl-aluminium et le nombre total de groupes alcoxy vaut 0,65/1, et l'on ajoute le chlorure d'alkyl-aluminium, éventuellement dilué dans un solvant de type hydrocarbure, à la suspension maintenue à une température de 30-35°C, puis on chauffe la suspension résultante à 60°C pendant 1 heure.
20. Procédé conforme à l'une des revendications précédentes, dans lequel le composant solide de catalyseur est un

EP 0 544 340 B1

solide qui se présente sous la forme de granules sphériques dont la taille va de 1 à 30 µm et dont la taille moyenne vaut de 7 à 15 µm, et qui présente une aire spécifique de 10 à 20 m²/g, une porosité de 65 à 85 % en volume et une masse volumique apparente de 0,4 à 0,5 g/ml, ainsi que la composition suivante, exprimée en proportions atomiques :

5



où R' représente un groupe alkyle linéaire ou ramifié, comportant de 1 à 5 atomes de carbone, et le titane se trouve en partie à l'état trivalent et en partie à l'état tétravalent, avec un rapport de 0,6/1 à 1/1 entre la quantité de titane trivalent et la quantité totale de titane.

- 10
21. Procédé conforme à l'une des revendications précédentes, dans lequel on maintient, au sein du catalyseur de type Ziegler-Natta, un rapport atomique de 5/1 à 400/1 entre l'aluminium et le titane.

15

 22. Procédé conforme à l'une des revendications précédentes, dans lequel le groupe alkyle du trialkyl-aluminium comporte de 2 à 6 atomes de carbone.
 23. Procédé conforme à la revendication 22, dans lequel le trialkyl-aluminium est un tributyl-aluminium.

20

25

30

35

40

45

50

55